ARKIV FÖR FYSIK Band 11 nr 11

Read 14 March 1956

On the connection between thermal expansion and potential energy in solids and liquids

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With 6 figures in the text

A recent investigation [1] on the density fluctuations in solids and liquids led to the formula

$$\frac{\Delta U}{\Delta V}=\frac{3}{2}\alpha. \tag{1}$$

Here ΔU is an increase in potential energy due to increased thermal fluctuations, ΔV the corresponding increase in volume, and α the pressure parameter in an equation of the form

$$(\Delta p+\alpha)(\Delta V+\beta)=\alpha\beta \tag{2}$$

describing the change ΔV in the volume, caused by a change Δp in the pressure. ΔU, ΔV and the volume parameter β are suitably referred to one mole of the substance.

In the quoted paper these equations were preliminarily tested by a calculation of α in three different ways, namely (i) from equation (1) applied to the increase of potential energy and volume at low temperatures, (ii) from the same equation applied to the change of energy and volume on fusion, and (iii) from equation (2) applied to the compressibility measurements of Bridgman and others. The test included ten metals of cubic structure and gave an encouraging approximate agreement.

In the present paper we shall make a more detailed test of equation (1) by confronting it with experimental data for some solid and liquid metals on the changes of potential energy and volume over the whole range of temperature where suitable data are available. The metals we have chosen to examine are the face-centered cubic metals Cu, Ag, Au, Al, and Pb, the body-centered cubic alkali metals Na and K, and the non-cubic metals Zn and Hg.

As a measure of the potential energy U at a temperature T°K we shall take the difference between the total energy

$$U_{\text{tot}}=\int_0^T C_p dT \tag{3}$$

obtained by integrating over the atomic heat C_p at constant, practically zero, pressure from 0 to T°K, and a suitable measure of the kinetic energy. At low temperature the kinetic energy will have to be half the total energy. At high temperature we shall assume that it approaches the classical value $3\,RT/2$ with increasing temperature. That is, we exclude for the metals rotational degrees of freedom. A function that will fulfil these conditions at least approximately is half of the Debye function for the internal energy

$$U_D = 3\,RT\left[3\left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{x^3}{e^x - 1}\,dx\right] \tag{4}$$

where θ is the Debye constant and the factor in brackets goes from 0 to 1 with increasing temperature. For $T > \theta$, U_D approximates to

$$U_D = 3RT - \frac{9}{8}R\,\theta \tag{5}$$

if the characteristic temperature θ is assumed to be a constant, independent of T. Our adopted measure of the potential energy will thus be

$$U = \int_0^T C_p\,dT - \frac{1}{2}U_D. \tag{6}$$

We assume this expression to be valid both for the solid and the liquid state, and we shall in the following compare it with the thermal increase in volume, including the change of total energy and of volume at the melting point.

For some metals the Debye function is not a very good approximation for the energy content at low temperatures, which also makes the choice of θ difficult. In such cases there may be an appreciable percental uncertainty in the calculated values of U at low temperatures. There is also a similar uncertainty in our knowledge of the changes of volume at very low temperatures. For the present, however, our main interest is concentrated on the range of temperature on both sides of the melting point. At these high temperatures a reasonable uncertainty in θ has no great importance. Thus we see from equations (5) and (6) that an error in θ of ten degrees would only cause a constant error in U of about ten calories per mole, which does not influence our conclusions.

Another minor uncertainty arises from the fact that we do not yet know how to apply the contribution from the free or magnetically active electrons to the energy content of the metals in our problem. However, the influence of this uncertainty is probably small as long as we do not include the ferromagnetic metals in our discussion.

The experimental data for the calculation of the total energy, which is needed in order to evaluate the potential energy from equation (6), have been obtained from the following sources. For the range of low temperatures from 0 to 300°K we have used for Cu, Ag, Al, Pb, K, and Zn the critical survey of Kelley [2] on C_p values from which the energy is obtained by graphical integration. For Au, Na, and Hg, we have used later results by Geballe and Giauque [3], Pickard and Simon [4], and Busey and Giauque [5]. For the range of temperature above 300°K we have used a very recent compilation by Stull and Sinke [6] for all the metals discussed.

For the Debye temperature θ we have chosen the values which other authors have found to be in the best agreement with the thermal energy or thermal expansion at low temperatures. The chosen values are given in the following tables which also contain the calculated values of potential energy in the last column.

As the thermal expansion has not generally been studied very well at the lowest temperatures, it seems preferable not to refer the changes of volume to the volume at absolute zero but to the volume at 0°C. The only usable compilation concerning thermal expansion that we have found is Kubaschewski's [7] on the percentage change of volume on fusion. Our other sources of information are as follows.

Cu.—The changes of volume in the solid state are taken from the X-ray measurements of Hume-Rothery and Andrews [8, 9], and those in the liquid state from the density measurements of Widawski and Sauerwald [10] compared with the density value $\varrho = 8.939$ at 0°C.

Ag.—The changes of volume in the solid state are from the X-ray measurements of Hume-Rothery and Reynolds [11, 9] and those in the liquid state from the density measurements of Jouniaux [12] compared with the value $\varrho = 10.511$ at 0°C.

Au.—The changes in the solid state (up to 730°C) are from the dilatometer measurements of Nix and MacNair [13]. The changes in the liquid state are from the density measurements of Krause and Sauerwald [14] (compared with $\varrho = 19.31$ at 0°C).

Al.—The low temperature values are from the dilatometer measurements of Nix and MacNair [12], those from 0°C to the melting point from the X-ray measurements of Wilson [15]. For the increase of volume on fusion is taken the value critically chosen by Kubachewski [7]. The relative changes of volume in the molten state are from the density measurements of Bornemann and Sauerwald [16].

Pb.—The volume changes below 0°C are from the dilatometer measurements of Nix and MacNair [17]. The expansions from 0 to 300°C are calculated from the results of dilatometer measurements by Eucken and Dannöhl [18]. The relative volumes of liquid lead are calculated from the density measurements of Day, Sosmann and Hostetter [19] and of Matuyama [20] compared with the value $\varrho = 11.337$ for 0°C. The densities from these two investigations show a nearly constant difference of about 0.2 per cent and we have taken the mean value.

Na.—The changes of volume below 0°C are calculated from the results of dilatometer measurements by Siegel and Quimby (21). From 0°C to the melting point at 97.2°C we have chosen mean values from different series of measurements reported in the Tables of Landolt-Börnstein. The change of volume at the melting point is that chosen by Kubaschewski [7]. On basis of the value thus obtained for liquid sodium at the melting point the volume changes in the liquid are obtained from the relative changes of density reported by Rinck [22].

K.—For potassium we have found no expansion measurements at low temperatures. The increase in volume from 0°C to the melting point at 63°C is taken from dilatometer measurements by Bernini and Cantoni [23], the increase on fusion is from the survey of Kubaschewski [7], and the relative changes in the liquid state from the density measurements of Rinck [22].

Zn.—The volume changes in the solid state are from a survey of Hume-Rothery [8] based on dilatometer measurements on single crystals by Grüneisen and Goens [24] and X-ray measurements by Owen and Yates [25]. The volume changes in the liquid state are calculated from the densities reported by Matuyama [20] compared with the value $\varrho = 7.195$ at 0°C.

Hg.—The most reliable density values for solid mercury are probably those obtained for single crystals at −191°C by Grüneisen and Sckell [26] and by X-ray measurements at −46°C by Mehl and Barrett [27]. The density of liquid mercury

Table 1.

Cu			Ag			Au		
$V_0 = 7.10$		$\theta = 325$	$V_0 = 10.25$		$\theta = 215$	$V_0 = 10.20$		$\theta = 190$
°C	$\frac{V - V_0}{V_0} \cdot 100$	$\frac{\text{cal}}{\text{mole}}$	°C	$\frac{V - V_0}{V_0} \cdot 100$	$\frac{\text{cal}}{\text{mole}}$	°C	$\frac{V - V_0}{V_0} \cdot 100$	$\frac{\text{cal}}{\text{mole}}$
− 186	− 0.78	64	− 180	− 0.91	114	− 173	− 0.68	156
101	0.46	263	100	0.53	300	73	0.30	439
0	0	559	0	0	632	0	0	662
+ 300	+ 1.56	1 500	+ 338	+ 2.08	1 773	+ 127	+ 0.54	1 067
500	2.80	2 195	459	2.89	2 223	327	1.45	1 737
671	3.90	2 834	596	3.86	2 754	527	2.43	2 442
771	4.53	3 228	724	4.84	3 294	727	3.53	3 188
871	5.24	3 637	846	5.87	3 794	1 063	—	4 584
1 084	—	4 547	943	6.74	4 223	1 063	—	7 550
1 084	—	7 670	961	—	4 321	1 100	12.0	7 690
1 110	12.9	7 790	961	—	6 980	1 200	12.8	8 090
1 200	14.0	8 250	970	12.8	7 000	1 300	13.6	8 500
1 300	15.2	8 640	990	13.0	7 090			
1 400	16.2	9 100	1 040	13.6	7 300			
1 500	17.3	9 550	1 145	14.9	7 750			
1 600	18.7	10 000	1 250	16.2	8 210			
			1 302	16.8	8 430			

Table 2.

Al			Pb		
$V_0 = 9.92$		$\theta = 398$	$V_0 = 18.25$		$\theta = 88$
°C	$\frac{V - V_0}{V_0} \cdot 100$	$\frac{\text{cal}}{\text{mole}}$	°C	$\frac{V - V_0}{V_0} \cdot 100$	$\frac{\text{cal}}{\text{mole}}$
− 173	− 0.98	62	− 173	− 1.41	211
73	0.47	287	73	0.61	524
0	0	497	0	0	767
+ 100	+ 0.71	813	+ 100	+ 0.88	1 113
200	1.51	1 145	200	1.88	1 477
300	2.32	1 506	300	3.07	1 865
400	3.22	1 893	327	—	1 971
500	4.19	2 308	327	6.4	3 070
600	5.26	2 752	400	7.3	3 390
659	5.89	3 017	500	8.5	3 800
659	12.3	5 520	600	9.8	4 220
700	12.8	5 690	700	11.0	4 630
800	14.2	6 100	800	12.3	5 040
900	15.6	6 500	900	13.5	5 430
1 000	16.9	6 900			

has been determined with high accuracy. Our values are taken from the tables of Landolt-Börnstein.

Corresponding values of the change in volume in per cent of the volume at 0°C and of the potential energy calculated according to equation (6) in calories per mole are listed in Tables 1 to 4.

Table 3.

Na			K		
$V_0=23.7$		$\theta=159$	$V_0=45.5$		$\theta=94$
°C	$\frac{V-V_0}{V_0}\cdot 100$	$\frac{\text{cal}}{\text{mole}}$	°C	$\frac{V-V_0}{V_0}\cdot 100$	$\frac{\text{cal}}{\text{mole}}$
−193	−3.51	115	0	0	835
173	3.25	163	+ 63	+1.58	1 118
123	2.42	311	63	4.2	1 720
73	1.49	473	127	6.0	1 950
0	0	735	227	9.0	2 380
+ 50	+0.97	932	327	12.2	2 800
97	2.15	1 120	427	15.5	3 210
97	4.7	1 800	527	19.0	3 630
200	7.8	2 230	627	22.8	4 050
300	11.0	2 650			
400	14.3	3 060			
500	17.9	3 470			
600	21.7	3 860			

Table 4.

Zn			Hg		
$V_0=9.09$		$\theta=206$	$V_0=14.75$		$\theta=96$
°C	$\frac{V-V_0}{V_0}\cdot 100$	$\frac{\text{cal}}{\text{mole}}$	°C	$\frac{V-V_0}{V_0}\cdot 100$	$\frac{\text{cal}}{\text{mole}}$
−180	−1.50	94	−191	−6.04	168
−100	0.88	294	46	4.53	641
0	0	589	39	—	669
+100	+0.89	901	39	0.69	1 224
200	1.82	1 253	0	0	1 363
300	2.78	1 618	+ 50	+0.91	1 550
350	3.29	1 805	100	1.83	1 730
419	3.97	2 062	150	2.75	1 910
419	9.7	3 850	200	3.68	2 090
451	10.4	3 990	250	4.63	2 260
494	11.3	4 190	300	5.59	2 440
539	12.0	4 490			
574	12.7	5 550			
619	13.3	4 750			
672	14.1	4 990			

For Cu, Ag, and Au, the data from Table 1 are plotted in Fig. 1 with potential energy as a function of the percentage changes of volume. In these metals with a high melting point there is an appreciable uncertainty in the liquid state both concerning the densities and the energies. Thus in the compilations we have used, only one constant value of the specific heat is given for the whole range of the liquid state, which is probably a very rough approximation.

Fig. 2 shows potential energy–volume diagrams for Al and Pb according to Table 2.

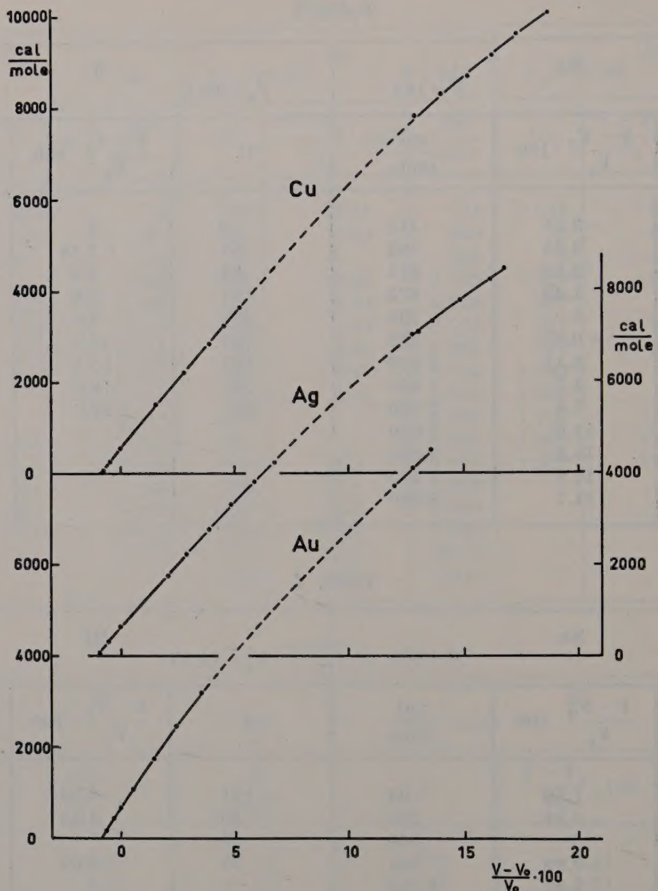

Fig. 1. Potential energy versus thermal change of volume for copper, silver and gold.

In the case of Pb the liquid states are known with somewhat better accuracy than for Cu, Ag, Au, and Al.

In the diagrams for all the face-centered cubic metals we have examined, the solid and liquid states can be connected by a common slightly bent curve. This is an exceedingly simple and illustrative support for the idea that fusion in uncomplicated cases is just a part of a transition beginning in the solid and continuing in the liquid state.

The bending of the curves means that the pressure parameter α, which according to equation (1) is obtained from the slopes of the curves, decreases with increasing volume. It is near at hand to try to connect this decrease of α with increasing volume with the increase of α with decreasing volume which appeared from the examination, in the foregoing paper [1] of Bridgman's compressibility data on sodium and potassium, and from the data on the dependence of the melting point on pressure. The only face-centered cubic metal for which we now have some useful data for a study of this kind is lead. Fig. 3 shows a plot of calculated α-values for lead against change

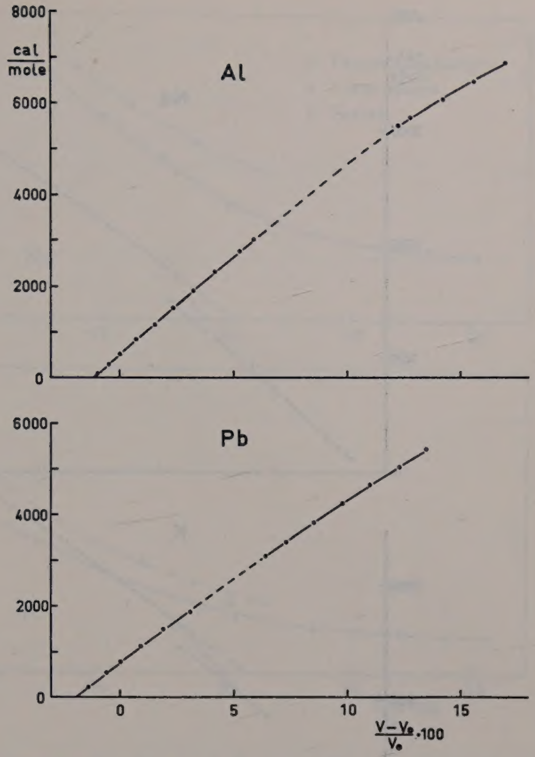

Fig. 2. Potential energy versus thermal change of volume for aluminium and lead.

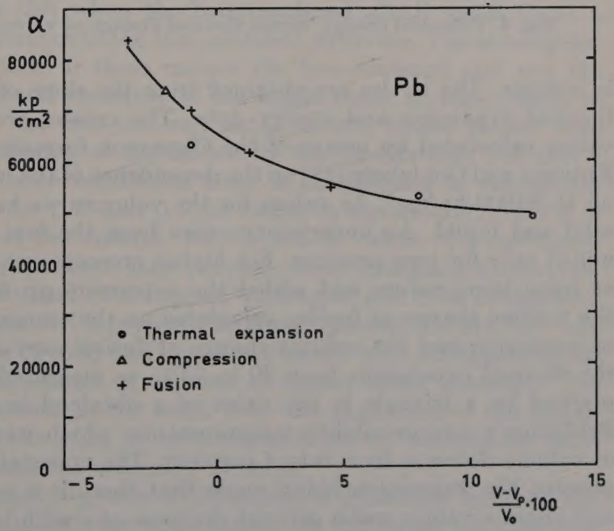

Fig. 3. Pressure parameter α versus percentage change of volume for lead.

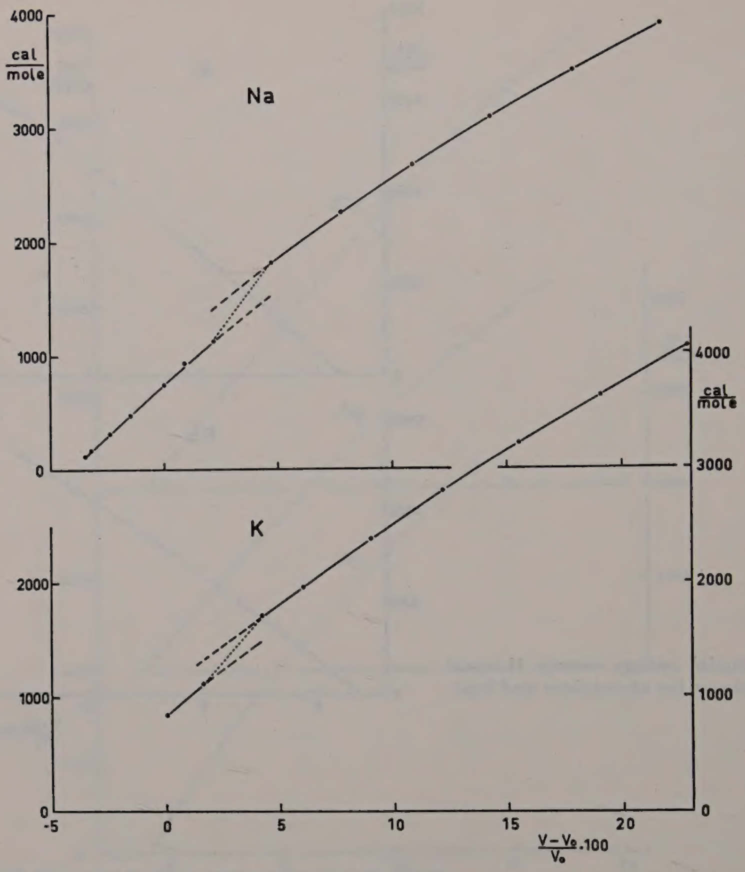

Fig. 4. Potential energy versus thermal change of volume for sodium and potassium.

in volume. The circles are obtained from the slope of the curve in Fig. 2, i.e. from thermal expansion and energy data. The crosses are obtained from the $\Delta U/\Delta V$ values calculated by means of the Clapeyron formula from recent measurements of Butusov and Gonigberg [28] on the dependence of the melting point of lead on pressure up to 30000 kp/cm^2. As values for the volumes we have taken the mean volume of solid and liquid. An uncertainty arises from the fact that these volumes are determined only for zero pressure. For higher pressures we have started from the volume at room temperature and added the expansion up to the melting point, and half the volume change at fusion, calculated on the assumption that both the coefficient of expansion and the volume change at fusion vary with pressure in proportion to the thermal expansions from 30 to 75°C, as measured by Bridgman [29]. The point marked by a triangle is the value of α obtained in the preceding paper [1] from Bridgman's compressibility measurements, which was in fact a mean over a range of volume decrease from 0 to 4 per cent. The uncertainties of the calculation cannot prevent the impression being made that there is a connection between all these α- and volume values and a general decrease of α with increasing volume.

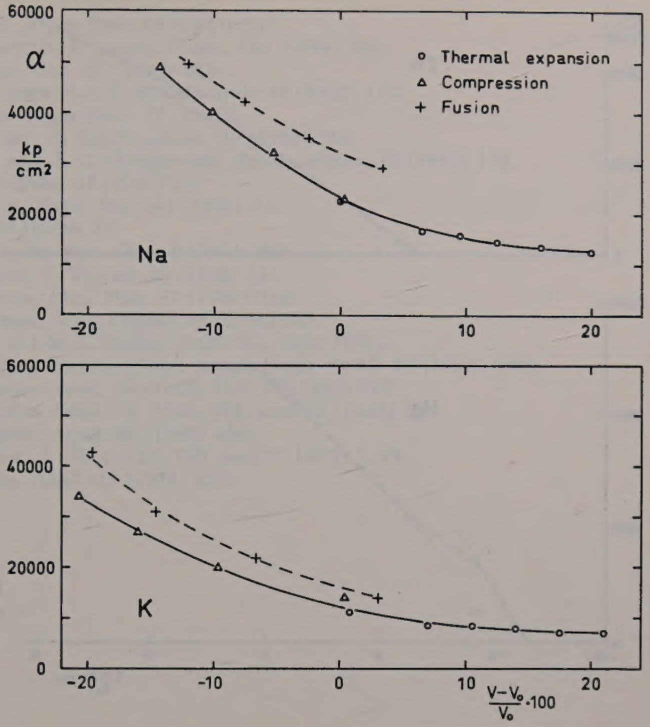

Fig. 5. Pressure parameter α versus percentage change of volume for sodium and potassium. Fusion data give wrong values.

Fig. 4 gives the energy–volume diagrams for Na and K according to the values in Table 3. For these body-centered cubic alkali metals the curves belonging to the solid and liquid states do not join. There is a discontinuity in volume of between one and two per cent. This discontinuity is of the same order as the decrease in volume observed by Bridgman [30] when the body-centered alkali metal Cs at a pressure of about 2300 kp/cm^2 changes to the face-centered structure. The assumption presents itself very naturally that in these metals the face-centered and not the body-centered structure is the basic structure of the liquid state. In these cases, as distinguished from the case of the face-centered cubic metals, fusion should thus involve not only the simple loosening of the lattice by the fluctuations but also a change of lattice structure. On such conditions there is no meaning in calculating α-values by inserting the values for ΔU and ΔV on fusion in equation (1). In Fig. 6 we have plotted, as a function of the volume, for Na and K values of α calculated by equation (1) from thermal expansion data (circles), from Bridgman's compressibility data for $p = 0$, 4000, 8000, and 12000 kp/cm^2 (triangles) and from Bridgman's melting-point data [31] by means of Clapeyron's formula (crosses). In the last case the volumes are the mean values of solid and liquid calculated from Bridgman's [32] data on thermal expansion and change of volume at fusion under pressure. The α-values obtained from the expansion of the solid, from the expansion of the liquid, and from the compressibility of the solid, lie on a common curve, whereas the false α-values obtained from fusion data are evidently too high.

For the non-cubic metals Zn and Hg, one could expect a difference between the structure of the lattice of the solid and the basic lattice for the liquid state causing

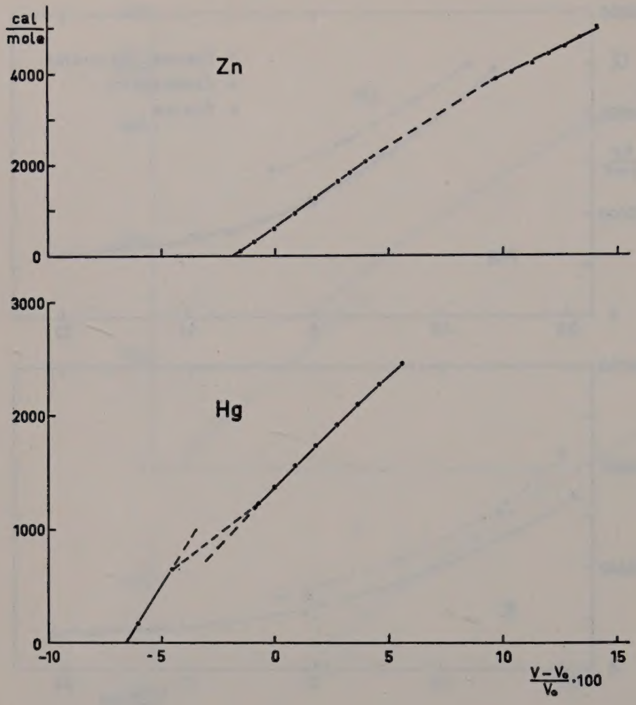

Fig. 6. Potential energy versus thermal change of volume for zinc and mercury.

a discontinuity between the curves in the U–V diagrams. As we see from Fig. 6 this discontinuity is, if it exists, not very pronounced for Zn. In the case of Hg on the other hand there seems to be no doubt about the existence of an appreciable discontinuity. We have good support for the general appearance of the diagram for Hg and the discontinuity also in the slope in the fact that the value of $\Delta U/\Delta V$ on fusion obtained from the diagram agrees well with the value obtained by means of Clapeyron's formula from Bridgman's data [33] on the variations of the melting point with pressure.

The author is indepted to Mr. L. E. Larsson for help with numerical work.

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Tryckt den 7 september 1956

Uppsala 1956. Almqvist & Wiksells Boktryckeri AB